

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 January 2002 (03.01.2002)

PCT

(10) International Publication Number
WO 02/00589 A2

- (51) International Patent Classification?: **C07C 67/00**
- (21) International Application Number: **PCT/JP01/05532**
- (22) International Filing Date: **27 June 2001 (27.06.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
2000-192964 27 June 2000 (27.06.2000) JP
60/218,803 18 July 2000 (18.07.2000) US
- (71) Applicant (for all designated States except US): **SHOWA DENKO K. K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **KADOWAKI, Et-suko** [JP/JP]; c/o Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **HIGASHI, Tomoyoshi** [JP/JP]; c/o Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **OGUCHI, Wataru** [JP/JP]; C/O Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **UCHIDA, Hiroshi** [JP/JP]; c/o Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP).
- (74) Agents: **ISHIDA, Takashi** et al.; A. Aoki, Ishida & Associates, Toranomon 37 Mori Bldg., 5-1, Toranomon 3-chome, Minato-ku, Tokyo 105-8423 (JP).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATALYST FOR USE IN PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER, PROCESS FOR PRODUCING THE CATALYST AND PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER USING THE CATALYST

(57) Abstract: A catalyst for use in producing a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising a step of contacting the catalyst with a gas containing at least one member selected from water, lower aliphatic carboxylic acids and lower aliphatic alcohols; a process for producing the catalyst; and a process for producing a lower aliphatic carboxylic acid ester using the catalyst. The catalyst can exhibit high initial activity and high space time yield, ensure sufficiently long catalyst life in practice in industry, and can prevent the production of by-product materials.

WO 02/00589 A2

DESCRIPTION

5 CATALYST FOR USE IN PRODUCING LOWER ALIPHATIC CARBOXYLIC
 ACID ESTER, PROCESS FOR PRODUCING THE CATALYST AND
 PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID
 ESTER USING THE CATALYST

Cross-Reference to Related Application

10 This application is an application filed under
35 U.S.C. §111(a) claiming benefit pursuant to
35 U.S.C. §119(e)(1) of the filing date of the
Provisional Application 60/218,803 filed July 18, 2000,
pursuant to 35 §111(b).

Technical Field

15 The present invention relates to a catalyst for use
in producing a lower aliphatic carboxylic acid ester from
a lower olefin and a lower aliphatic carboxylic acid, a
process for producing the catalyst, and a process for
producing a lower aliphatic carboxylic acid ester using
20 the catalyst.

More specifically, the present invention relates to
a catalyst for use in producing a lower aliphatic
carboxylic acid ester, which contains a specific
heteropolyacid salt and which is used in the process for
25 producing a lower aliphatic carboxylic acid ester by
esterifying a lower aliphatic carboxylic acid with a
lower olefin, wherein the catalyst is contacted with a
gas containing at least one member selected from the
group consisting of water, lower aliphatic carboxylic
30 acids and lower aliphatic alcohols before the reaction; a
process for producing the catalyst; and a process for
producing a lower aliphatic carboxylic acid ester using
the catalyst.

Background Art

35 It is well known that a corresponding ester can be
produced from a lower aliphatic carboxylic acid and an
olefin. Also, a catalyst comprising a heteropolyacid

- 2 -

and/or a salt thereof is known to effectively act in this reaction. Specific examples of such a catalyst include those described in Japanese Unexamined Patent Publications No. 4-139148 (JP-A-4-139148), No. 4-13949 (JP-A-4-139149), No. 5-65248 (JP-A-5-65248) and No. 5-294894 (JP-A-5-294894).

Among these specific examples, the catalysts containing at least one salt selected from the group consisting of cesium salts, rubidium salts, thallium salts, ammonium salts and potassium salts of phosphotungstic acid, silicotungstic acid, phosphomolybdic acid and silicomolybdic acid disclosed in JP-A-4-139148, JP-A-4-139149 and JP-A-5-65248, exhibit high initial activity and relatively high space time yield. However, in use on an industrial base, for example, the activity decreases and the space time yield also lowers with the progress of reaction and this was a problem to be solved.

In order to solve this problem, Japanese Unexamined Patent Publication No. 5-170698 (JP-A-5-170698) proposes a method of contacting a catalyst described above with water and an organic carboxylic acid or an organic carboxylic acid ester in a gas phase before performing the reaction. In a production process of a lower aliphatic carboxylic acid ester using a catalyst subjected to a pre-contacting treatment according to the above-described method, it is revealed that the catalyst exhibits high initial activity and the activity scarcely decreases as compared with conventional production processes using a catalyst which is not subjected to the contacting treatment.

On the other hand, Japanese Unexamined Patent Publication No. 5-294894 (JP-A-5-294894) discloses a catalyst obtained by loading at least one heteropolyacid salt selected from the group consisting of lithium salts, copper salts, magnesium salts and gallium salts of heteropolyacids on a support and it is revealed that

although the method disclosed in JP-A-5-170698 of contacting a catalyst with water and an organic carboxylic acid or an organic carboxylic acid ester in a gas phase before performing the reaction is not used, the catalyst can exhibit initial activity equal thereto or higher than that and can maintain the activity.

In other words, with respect to the initial activity and space time yield of the catalyst and the maintenance thereof (so-called catalyst life), the problems have been overcome by the catalyst disclosed in JP-A-5-294894. The matter in need of improvement is the production of by-products such as olefins, having 3 or more carbon atoms including butene, and aldehydes.

The production of these by-products directly causes reduction in the selectivity of reaction. Furthermore, these by-products sometimes become catalyst poisons in the reaction of a lower olefin with a lower aliphatic carboxylic acid and may conspicuously inhibit the reaction.

Particularly, in industrially performing the process for producing a lower aliphatic carboxylic acid ester through the reaction, a circulation process is generally employed mainly for recycling unreacted raw materials so as to increase the reaction efficiency in view of profitability. In this case, if those by-products are not removed and returned to a reaction system via a circulation system, the catalyst may be damaged and the catalyst life greatly shortened.

To solve this problem, the methods described, for example, in Japanese Unexamined Patent Publications No. 11-269126 (JP-A-11-269126) and No. 11-335323 (JP-A-11-335323) may be used. JP-A-11-269126 discloses a method of removing acetaldehyde impurities at the reactor inlet by distillation or by reacting them with a compound highly reactive with an aldehyde group. Also, JP-A-11-335323 discloses a method of newly providing a step for removing acetaldehyde using an acetaldehyde-removing

column and thereby separating it. In either case, however, a new separation step must be provided, therefore, the process becomes very cumbersome and the costs increase.

5 As such, it has been proposed to provide a step for separating and removing by-products so that the catalyst life can be maintained even in the process employing a circulation system. However, means to solve this problem from the standpoint of sufficiently suppressing the
10 production of by-products themselves in the reaction has not yet been found.

Disclosure of Invention

 The object of the present invention is to provide a catalyst for use in producing a lower aliphatic
15 carboxylic acid ester, which is used in producing a lower aliphatic carboxylic acid ester from a lower olefin and a lower aliphatic carboxylic acid and which is a catalyst having high initial activity and high space time yield, favored with a catalyst life long enough to endure
20 practical use in industry and capable of reducing the production of by-products; a process for producing the catalyst; and a process for producing a lower aliphatic carboxylic acid ester using the catalyst.

 The present inventors have made extensive
25 investigations into a catalyst not only capable of exhibiting high initial activity and sufficiently long catalyst life at the reaction of a lower olefin and a lower aliphatic carboxylic acid in a gas phase to produce a lower fatty acid ester, but also reduced in the
30 production of by-products represented by butene and aldehydes which work out to a catalyst poison. As a result, it has been found that when a specific step is provided in the preparation of a catalyst, the catalyst can be greatly reduced in the production of by-products harmful to the catalyst, such as butene and aldehydes.
35 The present invention has been accomplished based on this finding.

More specifically, the present invention (I) is a catalyst for use in producing a lower aliphatic carboxylic acid ester, which is used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

The present invention (II) is a process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, the catalyst being used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

The present invention (III) is a process for

producing a lower aliphatic carboxylic acid ester,
comprising reacting a lower olefin with a lower aliphatic
carboxylic acid in a gas phase in the presence of the
catalyst for use in producing a lower aliphatic
5 carboxylic acid ester of the present invention (I).

The present invention (IV) is a process for
producing a lower aliphatic carboxylic acid ester
comprising reacting a lower olefin with a lower aliphatic
carboxylic acid in a gas phase, which process comprises
10 the following first to fourth steps:

First Step

a step for loading one or more heteropolyacid salts
on a support to obtain a heteropolyacid salt supported
catalyst;

15 Second Step

a step of filling the heteropolyacid salt supported
catalyst obtained in the first step, into a reactor for
use in the reaction of the lower olefin with the lower
aliphatic carboxylic acid in a gas phase;

20 Third Step

a step of contacting the heteropolyacid salt
supported catalyst filled in the reactor, with a gas
containing at least one member selected from the group
consisting of water, lower aliphatic carboxylic acids and
25 lower aliphatic alcohols; and

Fourth Step

a step of passing a mixed gas containing the lower
olefin and the lower aliphatic carboxylic acid through
the heteropolyacid salt supported catalyst after the
30 third step, to obtain the lower aliphatic carboxylic acid
ester.

Best Mode for Carrying Out the Invention

The present invention will be described below with
reference to preferred embodiments thereof.

35 The present invention (I) is a catalyst for use in
producing a lower aliphatic carboxylic acid ester, which
is used in reacting a lower olefin with a lower aliphatic

carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

5 First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

10 a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use
15 in producing a lower aliphatic carboxylic acid ester.

That is, the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) is a catalyst obtained by a production process comprising the above-described first and second steps.

20 The first step is described below.

In the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I), the heteropolyacid used in the first step comprises a center element and a peripheral element to which oxygen
25 is bonded. The center element is usually silicon or phosphorus but may comprise an optional element selected from various kinds of elements belonging to Groups I to XVII of the Periodic Table.

Specific examples of the center element include
30 cupric ion; divalent beryllium, zinc, cobalt and nickel ions; trivalent boron, aluminum, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium and rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulfur, tellurium,
35 manganese, nickel, platinum, thorium, hafnium and cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium and antimony ions; hexavalent tellurium

ion; and heptavalent iodide ion, however, the present invention is by no means limited thereto. Specific examples of the peripheral element include tungsten, molybdenum, vanadium, niobium and tantalum, however, the present invention is by no means limited thereto.

These heteropolyacids are also known as a "polyoxo-anion", a "polyoxometallic salt" or a "metal oxide cluster". Some well known structures of anions are named after a researcher himself in this field, for example, as Keggin, Wells-Dawson or Anderson-Evans-Perloff structures. There are detailed description in "Porisan no Kagaku, Kikan Kagaku Sousetau (Chemistry of Polyacids, Seasonal Publication for Introduction to Chemistry)", No. 20, 1993, edited by Japan Chemical Society.

Heteropolyacids usually have a high molecular weight, for example, a molecular weight of 700 to 8,500, and include dimeric complexes.

Specific examples of the heteropolyacid which can be used as the starting material of heteropolyacid salt in the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) include:

Tungstosilicic acid	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
Tungstophosphoric acid	$H_3[PW_{12}O_{40}] \cdot xH_2O$
Molybdophosphoric acid	$H_3[PMo_{12}O_{40}] \cdot xH_2O$
Molybdosilicic acid	$H_4[SiMo_{12}O_{40}] \cdot xH_2O$
Vanadotungstosilicic acid	$H_{4+n}[SiVW_{12-n}O_{40}] \cdot xH_2O$
Vanadotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdophosphoric acid	$H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdosilicic acid	$H_{4+n}[SiV_nMo_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstosilicic acid	$H_{4+n}[SiMo_nW_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$

wherein n is an integer of 1 to 11 and x is an integer of at least 1. However, the present invention is by no means limited thereto.

Among these, preferred are tungstosilicic acid, tungstophosphoric acid, molybdophosphoric acid, molybdo-

silicic acid, vanadotungstosilicic acid and
vanadotungstophosphoric acid, and more preferred are
tungstosilicic acid, tungstophosphoric acid,
vanadotungstosilicic acid and vanadotungstophosphoric
5 acid.

The method of the production of the heteropolyacids
are not particularly limited and any methods can be used.
For example, they may be produced by heating an acidic
aqueous solution (a pH of about 1-2) containing a salt of
10 molybdec acid or tungstic acid and a simple oxygen acid
of a hetero-atom or a salt thereof. A heteropolyacid
compound may be isolated from the resulting aqueous
heteropolyacid solution by a method of separation through
precipitation as a metal salt, for example. Specific
15 examples are described in "Shin Jikken Kagaku Kouza 8,
Muki Kagoubutsu no Gousei (III) (New Experimental
Chemistry Course 8, Synthesis of Inorganic Compounds)",
edited by Japan Chemical Society, published by Maruzen
K.K., August 20, 1984, Third Edition, page 1413, but the
20 present invention is by no means limited thereto. The
Kiggin structure of the obtained heteropolyacid can be
confirmed by chemical analysis as well as X-ray
diffraction, UV and IR measurements.

The heteropolyacid salt as used in the catalyst for
25 use in producing a lower aliphatic carboxylic acid ester
of the present invention (I) is not particularly limited
as long as it is a metal salt or an onium salt in which a
part or all of hydrogen atoms of the above-described
heteropolyacids are substituted. Specific examples
30 thereof include salts of metals such as lithium, sodium,
magnesium, barium, copper, gold and gallium, and onium
salts, however, the present invention is not limited
thereto. Among these, preferred are lithium salts,
sodium salts, gallium salts, copper salts and gold salts,
35 more preferred are lithium salts, sodium salts and copper
salts.

Heteropolyacids have a relatively high solubility in

a polar solvent such as water and other oxygen-containing solvents particularly when the heteropolyacids are free acids or comprise several salts, and the solubility can be controlled by appropriately selecting the counter ion.

5 Examples of the starting material for the metal element or onium moiety of forming the heteropolyacid salt in the present invention include lithium nitrate, lithium acetate, lithium sulfate, lithium sulfite, lithium carbonate, lithium phosphate, lithium oxalate,
10 lithium nitrite, lithium chloride, lithium citrate, sodium nitrate, sodium acetate, sodium sulfate, sodium carbonate, monosodium phosphate, disodium phosphate, sodium oxalate, sodium nitrite, sodium chloride, sodium citrate, magnesium nitrate hexahydrate, magnesium acetate
15 tetrahydrate, magnesium sulfate, magnesium carbonate, magnesium phosphate tricosahydrate, magnesium oxalate dihydrate, magnesium chloride, magnesium citrate, barium nitrate, barium acetate, barium sulfate, barium carbonate, barium hydrogenphosphate, barium oxalate
20 monohydrate, barium sulfite, barium chloride, barium citrate, copper nitrate, copper acetate, copper sulfate, copper carbonate, copper diphosphate, copper oxalate, copper chloride, copper citrate, aurous chloride, chloroauric acid, auric oxide, auric hydroxide, auric
25 sulfide, aurous sulfide, gallium dichloride, gallium monochloride, gallium citrate, gallium acetate, gallium nitrate, gallium sulfate, gallium phosphate, ammonium acetate, ammonium carbonate, ammonium nitrate, ammonium dihydrogenphosphate, ammonium hydrogencarbonate, ammonium
30 citrate, ammonium nitrate, diammonium phosphate, monoammonium phosphate and ammonium sulfate, however, the present invention is by no means limited thereto.

 Among these, preferred are lithium nitrate, lithium acetate, lithium carbonate, lithium oxalate, lithium
35 citrate, sodium nitrate, sodium acetate, sodium carbonate, sodium oxalate, sodium citrate, copper nitrate, copper acetate, copper carbonate, copper

citrate, aurous chloride, chloroauric acid, gallium
citrate, gallium acetate and gallium nitrate, and more
preferred are lithium nitrate, lithium acetate, lithium
carbonate, lithium oxalate, lithium citrate, sodium
5 nitrate, sodium acetate, sodium carbonate, sodium
oxalate, sodium citrate, copper nitrate, copper acetate,
copper carbonate and copper citrate.

Specific examples of the heteropolyacid salt which
can be used in the catalyst for use in producing a lower
10 aliphatic carboxylic acid ester of the present invention
(I) include lithium salt of tungstosilicic acid, sodium
salt of tungstosilicic acid, copper salt of
tungstosilicic acid, gold salt of tungstosilicic acid,
gallium salt of tungstosilicic acid, lithium salt of
15 tungstophosphoric acid, sodium salt of tungstophosphoric
acid, copper salt of tungstophosphoric acid, gold salt of
tungstophosphoric acid, gallium salt of tungstophosphoric
acid, lithium salt of molybdophosphoric acid, sodium salt
of molybdophosphoric acid, copper salt of
20 molybdophosphoric acid, gold salt of molybdophosphoric
acid, gallium salt of molybdophosphoric acid, lithium
salt of molybdosilicic acid, sodium salt of
molybdosilicic acid, copper salt of molybdosilicic acid,
gold salt of molybdosilicic acid, gallium salt of
25 molybdosilicic acid, lithium salt of vanadotungstosilicic
acid, sodium salt of vanadotungstosilicic acid, copper
salt of vanadotungstosilicic acid, gold salt of
vanadotungstosilicic acid, gallium salt of
vanadotungstosilicic acid, lithium salt of
30 vanadotungstophosphoric acid, sodium salt of
vanadotungstophosphoric acid, copper salt of
vanadotungstophosphoric acid, gold salt of
vanadotungstophosphoric acid, gallium salt of
vanadotungstophosphoric acid, lithium salt of
35 vanadomolybdophosphoric acid, sodium salt of
vanadomolybdophosphoric acid, copper salt of
vanadomolybdophosphoric acid, gold salt of

vanadomolybdophosphoric acid, gallium salt of
vanadomolybdophosphoric acid, lithium salt of
vanadomolybdosilicic acid, sodium salt of vanadomolybdo-
silicic acid, copper salt of vanadomolybdosilicic acid,
5 gold salt of vanadomolybdosilicic acid and gallium salt
of vanadomolybdosilicic acid.

Among these, preferred are lithium salt of
tungstosilicic acid, sodium salt of tungstosilicic acid,
copper salt of tungstosilicic acid, gold salt of
10 tungstosilicic acid, gallium salt of tungstosilicic acid,
lithium salt of tungstophosphoric acid, sodium salt of
tungstophosphoric acid, copper salt of tungstophosphoric
acid, gold salt of tungstophosphoric acid, gallium salt
of tungstophosphoric acid, lithium salt of
15 molybdophosphoric acid, sodium salt of molybdophosphoric
acid, copper salt of molybdophosphoric acid, gold salt of
molybdophosphoric acid, gallium salt of molybdophosphoric
acid, lithium salt of molybdosilicic acid, sodium salt
of molybdosilicic acid, copper salt of molybdosilicic
20 acid, gold salt of molybdosilicic acid, gallium salt of
molybdosilicic acid, lithium salt of vanadotungstosilicic
acid, sodium salt of vanadotungstosilicic acid, copper
salt of vanadotungstosilicic acid, gold salt of
vanadotungstosilicic acid, gallium salt of
25 vanadotungstosilicic acid, lithium salt of
vanadotungstophosphoric acid, sodium salt of
vanadotungstophosphoric acid, copper salt of
vanadotungstophosphoric acid, gold salt of
vanadotungstophosphoric acid and gallium salt of
30 vanadotungstophosphoric acid.

More preferred are lithium salt of tungstosilicic
acid, sodium salt of tungstosilicic acid, copper salt of
tungstosilicic acid, gold salt of tungstosilicic acid,
gallium salt of tungstosilicic acid, lithium salt of
35 tungstophosphoric acid, sodium salt of tungstophosphoric
acid, copper salt of tungstophosphoric acid, gold salt of
tungstophosphoric acid, gallium salt of tungstophosphoric

acid, lithium salt of vanadotungstosilicic acid, sodium salt of vanadotungstosilicic acid, copper salt of vanadotungstosilicic acid, gold salt of vanadotungstosilicic acid, gallium salt of vanadotungstosilicic acid, lithium salt of vanadotungstophosphoric acid, sodium salt of vanadotungstophosphoric acid, copper salt of vanadotungstophosphoric acid, gold salt of vanadotungstophosphoric acid and gallium salt of vanadotungstophosphoric acid.

In the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I), the heteropolyacid salt as a catalytic activity component is supported on a support. Substances which can be used as the support are not particularly limited and porous substances commonly used as a support may be used. Specific examples thereof include those comprising silica, diatomaceous earth, montmorillonite, titania, activated carbon, alumina and silica alumina, preferably silica, silica alumina and montmorillonite.

The support is also not limited on the shape thereof and may be in the powder, spherical, pellet-like or any other form. A sphere or pellet-like form is preferred. Furthermore, the particle size is not particularly limited and although the preferred particle size varies depending on the reaction form, the average diameter is preferably from 2 to 10 mm in the case of use in a fixed bed system and from powder to 5 mm in the case of use in a fluidized bed system.

The support is most preferably a spherical or pellet-form siliceous support.

The method for loading the heteropolyacid salt on the support in the first step of the catalyst for producing a lower aliphatic carboxylic acid ester of the present invention (I) is roughly classified into the following three groups (1) to (3).

(1) A method of loading a desired heteropolyacid on a support and thereafter loading a starting material for

- 14 -

the desired element or moiety of forming the salt.

(2) A method of loading a desired heteropolyacid together with a starting material for the element or moiety of forming the salt or loading a previously prepared heteropolyacid salt on a support.

(3) A method of previously loading a starting material for the element or moiety of forming the salt on a support and thereafter loading a desired heteropolyacid thereon.

In any of these methods (1) to (3), the heteropolyacid and the starting material for the element or moiety of forming the salt each can be loaded by dissolving or suspending it in an appropriate solvent. The solvent may be any as long as it can uniformly dissolve or suspend the desired heteropolyacid, a salt thereof and the starting material for the element or moiety of forming the salt, and examples of the solvent which can be used include water, an organic solvent and a mixture thereof. Among these, preferred are water, alcohols and carboxylic acids.

The method used for the dissolution or suspension may also be any as long as it can uniformly dissolve or suspend the desired heteropolyacid, a salt thereof and the starting material for the element or moiety of forming the salt. In the case of a free acid, a free acid which can dissolve may be dissolved as it is in a solvent and even in the case of a free acid which cannot completely dissolve, if the free acid can be uniformly suspended by forming it into fine powder, the free acid may be suspended as such.

In the method (1), a solution or suspension obtained by dissolving or suspending a heteropolyacid in a solvent is absorbed to a support to thereby load the heteropolyacid on the support and, then, a solution or suspension of a starting material for the element or moiety of forming a desired salt is absorbed to the support to thereby load the element or moiety. At this

time, a neutralization reaction proceeds on the support, as a result, a heteropolyacid salt supported catalyst can be prepared.

5 In the method (2), a heteropolyacid and a starting material for the element or moiety of forming the salt are dissolved or suspended together or separately and then mixed to prepare a uniform solution or suspension, and the solution or suspension is absorbed to a support, thereby loading the heteropolyacid and the element or
10 moiety. In the case of a compound in the state of a heteropolyacid salt, a uniform solution or suspension may be obtained in the same manner as in the case of a free acid.

15 In the method (3), a solution or suspension of a starting material for the element or moiety of forming the salt is previously prepared, the solution or suspension is absorbed to a support to thereby load the element or moiety, and then a desired heteropolyacid is loaded. This method includes a method of using an
20 element or moiety which is previously contained in the support and which can form a heteropolyacid salt.

More specifically, a part or all of the elements previously contained in a support sometimes act to form a salt of a heteropolyacid when the heteropolyacid is
25 loaded, and as a result, a heteropolyacid salt is formed. Examples of such an element include potassium, sodium, calcium, iron, magnesium, titanium and aluminum, however, the present invention is not limited thereto.

The kind of the element previously contained in a
30 support and the amount thereof can be determined by a chemical analysis such as inductively coupled plasma emission spectrometry (hereinafter referred to as "ICP"), fluorescent X-ray method and atomic absorption method. The kind and the amount of the element vary depending on
35 the support, however, potassium, sodium, calcium, iron, magnesium, titanium and aluminum are sometimes contained in a relatively large amount and the content thereof is

approximately from 0.001 to 5.0% by mass. Therefore, depending on the combination of a support and a heteropolyacid, the element previously contained in the support may be in an amount large enough to form a salt, though this may vary depending on the kind and the amount of the heteropolyacid to be supported.

The method for loading a solution or suspension of heteropolyacid or a salt thereof on a support is not particularly limited and a known method may be used. Specifically, for example, the catalyst may be prepared by dissolving a heteropolyacid in a distilled water corresponding to the liquid absorption amount of the support used and impregnating the solution into a support. Also, the catalyst may be prepared using an excess aqueous heteropolyacid solution by impregnating it into a support while appropriately moving the support in the heteropolyacid solution and then removing the excess acid by filtration. The volume of the solution or suspension used at this time varies depending on the support used or the loading method thereon.

The thus-obtained wet catalyst is suitably dried by placing it in a heating oven for a few hours. The drying method is not particularly limited and any method such as of a standing or belt conveyor system may be used. After drying, the catalyst is cooled to the ambient temperature in a desiccator so as not to absorb moisture.

The amount of the heteropolyacid salt supported in the heteropolyacid salt supported catalyst can be simply calculated by subtracting the weight of the support used from the weight after drying of the catalyst prepared. The amount supported may be more exactly determined by a chemical analysis such as ICP, fluorescent X-ray method or atomic absorption method.

The amount of the heteropolyacid salt supported is preferably from 10 to 150% by mass, more preferably from 30 to 100% by mass, based on the entire weight of the support.

If the heteropolyacid salt content is less than 10% by mass, the content of active components in the catalyst is too small and the activity per the catalyst unit weight may disadvantageously decrease. If the
5 heteropolyacid salt content exceeds 150% by mass, the effective pore volume may decrease, as a result, the effect owing to the increase in the supported amount may not be brought out and at the same time, coking may be disadvantageously liable to occur to greatly shorten the
10 catalyst life.

The second step is described below.

The second step in the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) is a step for contacting the heteropolyacid
15 salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

The term "contacting" as used above refers to
20 bringing the heteropolyacid salt supported catalyst obtained in the first step into contact with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols. The method for the contacting
25 is not particularly limited and for example, the following methods may be used.

(a) A method of placing the heteropolyacid salt supported catalyst obtained in the first step in an atmosphere of a gas containing at least one member
30 selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

(b) A method of passing a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic
35 alcohols through the heteropolyacid salt supported catalyst obtained in the first step.

(c) A method of passing the heteropolyacid salt

supported catalyst obtained in the first step, through an atmosphere of a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

5 These methods may be used in combination of two or more thereof.

 To speak more specifically on the method of performing the second step, for example, a method of filling the supported catalyst obtained in the first step
10 into a vessel and contacting the gas therewith, or a method of filling the supported catalyst obtained in the first step into, in place of the vessel, a reactor where the production process of a lower aliphatic carboxylic acid ester is performed later, and contacting the gas
15 therewith before feeding reaction starting materials, may be used.

 With respect to the shape of the vessel or the reactor used here, any shape such as vertical type or horizontal type may be used without any particular limit.

20 In view of the time to be spent for re-filling the catalyst or the vessel cost, the preferred embodiment of the second step includes a method of filling the supported catalyst obtained in the first step into a reactor which is used in reacting a lower olefin with a
25 lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, and then contacting therewith a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols
30 before feeding the reaction starting materials. At this time, the reaction may be performed in either a closed circulatory system or a flow system.

 The second step is preferably performed under conditions not less than the dew point of the gas
35 containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols. If the conditions are less

than the dew point of the gas, a part of the gas may turn into a liquid. In this case, the heteropolyacid salt supported on the catalyst in the first step or other catalyst components supported, as desired, may dissolve out to change the catalyst composition, and in the worst case, the catalyst may be deactivated. As long as the catalyst is not adversely affected, the conditions in performing the second step are not particularly limited.

The preferred embodiment of the conditions at the dew point or more of the gas may vary depending on the composition of the gas or the pressure or the like in the practice of the step, however, the contact temperature is preferably from 80 to 300°C, more preferably from 100 to 260°C.

The contact pressure is not particularly limited and may be either normal pressure or raised pressure. The contact pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The lower aliphatic carboxylic acid in a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step, is preferably a lower aliphatic carboxylic acid having from 1 to 6 carbon atoms. Specific examples thereof include formic acid, acetic acid, propionic acid, n-butyric acid and isobutyric acid. Among these, preferred are acetic acid and propionic acid.

The lower aliphatic alcohol in a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is preferably a lower aliphatic alcohol having from 1 to 6 carbon atoms. Specific examples thereof include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol. Among these, preferred are methanol, ethanol and n-propanol.

The composition of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is not particularly limited, and
5 water, a lower aliphatic carboxylic acid and a lower aliphatic alcohol can be mixed at any ratio. The composition is preferably such that water : a lower aliphatic carboxylic acid : a lower aliphatic alcohol = 1.0 : 0.1-10.0 : 0.1-5.0 by molar ratio.

10 The composition of the gas may be constant from the beginning to the end of contacting or may vary according to the contacting time or the stage of contacting.

The gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic
15 acids and lower aliphatic alcohols used in the second step is more preferably water alone or a mixed gas of water and acetic acid, still more preferably a mixed gas of water and acetic acid because the effect can be provided within a short time.

20 In the case of using a mixed gas of water and acetic acid as the gas, the composition is not particularly limited but preferably such that water : acetic acid = 1.0 : 0.1-10.0, more preferably water : acetic acid = 1.0 : 0.5-5.0, by molar ratio.

25 The gas hourly space velocity (hereinafter referred to as "GHSV"), which is the speed of feeding the gas in performing the contact with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols
30 used in the second step, is not particularly limited. The GHSV is preferably from 100 to 7,000 hr⁻¹, more preferably from 300 to 3,000 hr⁻¹.

If the GHSV is too high, the amount of the gas used may increase and this is not preferred in view of the
35 cost. From this standpoint, the contacting may also be performed by feeding a constant amount of the gas and enclosing it in a vessel.

The contacting time is not particularly limited, however, it is preferably from 0.5 to 200 hours, more preferably from 0.5 to 100 hours, and most preferably from 0.5 to 50 hours. The optimal time varies depending on the composition and concentration of the gas, the temperature and pressure at the contacting, and the catalyst component.

Generally, if the contacting time is less than 0.5 hours, the effect of the second step may not be fully brought out, whereas if the contacting time is prolonged, the effect may be liable to increase but even if the contacting time is prolonged to exceed 200 hours, the effect may not increase any more, moreover, in the case where gas is contacted in the flowing state, the amount of the gas used may increase and this is not preferred in view of the profitability.

The present invention (II) is described below. The present invention (II) is a process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, the catalyst being used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step for contacting the heteropolyacid salt supported catalyst obtained at the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for use in producing a lower aliphatic carboxylic acid ester.

The heteropolyacid salt and the support used in the first step, the method for loading the heteropolyacid

salt on a support performed in the first step, the method for measuring the amount of the heteropolyacid salt supported, and the preferred amount of the heteropolyacid salt supported on a support may be the same as in the present invention (I).

Furthermore, the method for contacting the catalyst with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols performed in the second step, the conditions therefor such as temperature, pressure, GHSV and time, the lower aliphatic carboxylic acid and lower aliphatic alcohol used for the gas, and the compositional ratio of the gas to which water is further added, may be the same as in the present invention (I).

In the process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (II), as long as the following first and second steps are contained, other steps may be provided before, after or during these steps, if desired.

First Step

A step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst.

Second Step

A step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for use in producing a lower aliphatic carboxylic acid ester.

Examples of the step which is provided, as desired, include a step for loading a third component so as to more improve the catalytic activity. In such a case, this loading operation may be performed simultaneously with the operation of loading the heteropolyacid salt in the first step, if possible.

After the second step of contacting with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, the catalyst may further be
5 contacted with another gas.

The present invention (III) is described below. The present invention (III) is a process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic
10 acid in a gas phase in the presence of the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I).

In the process for producing a lower aliphatic carboxylic acid ester of the present invention (III), a
15 gas phase reaction is not particularly limited on the reaction form and the reaction may be performed in any form such as in a fixed bed system or fluidized bed system. The shape of the support which governs the shape or size of the catalyst may be selected in the range from
20 powder to a compact formed into a size of several mm according to the reaction form employed.

Examples of the lower olefin which can be used in the process for producing a lower aliphatic carboxylic acid ester of the present invention (III), include
25 ethylene, propylene, n-butene, isobutene and a mixture of two or more thereof.

The lower aliphatic carboxylic acid is suitably a carboxylic acid having from 1 to 4 carbon atoms and specific examples thereof include formic acid, acetic
30 acid, propionic acid, butyric acid, acrylic acid and methacrylic acid.

The ratio between the lower olefin and the lower aliphatic carboxylic acid used as the starting materials is not particularly limited. In view of the conversion
35 of the lower olefin, the lower olefin is preferably used in an equimolar or excess amount based on the lower aliphatic carboxylic acid. Specifically, the molar ratio

of the lower olefin to the lower aliphatic carboxylic acid is preferably in the range of lower olefin : a lower aliphatic carboxylic acid = from 1:1 to 30:1, more preferably from 3:1 to 20:1, still more preferably from 5:1 to 15:1.

Furthermore, from the standpoint of maintaining the catalytic activity, a small amount of water is preferably added to the starting materials. However, if an excessively large amount of water is added, the amount of a by-product such as an alcohol or an ether may disadvantageously increase. The amount of water added is preferably from 0.5 to 15 mol%, more preferably from 2 to 8 mol%, in terms of the molar ratio of water to the total amount of the lower olefin, the lower aliphatic carboxylic acid, as the starting materials, and water added.

The reaction conditions such as temperature and pressure preferred in the process for producing a lower aliphatic carboxylic acid ester of the present invention (III), may vary depending on the lower olefin and the lower aliphatic carboxylic acid used as the starting materials. The reaction conditions such as temperature and pressure are preferably combined so that the starting materials each can be kept in the gas state and the reaction can satisfactorily proceed.

In general, the temperature is preferably from 120 to 300°C, more preferably from 140 to 250°C. The pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The starting materials each is not particularly limited on the GHSV. If the GHSV is excessively high, the gas may pass through before the reaction satisfactorily proceeds, whereas if it is too low, problems, such as reduction in the productivity, may arise. The GHSV is preferably from 100 hr⁻¹ to 7,000 hr⁻¹, more preferably from 300 hr⁻¹ to 3,000 hr⁻¹.

The unreacted lower olefin and also alcohol and

ether produced as by-products in the reaction may be recycled and used as they are. At this time, the substances which are harmful to the catalyst for use in producing a lower aliphatic carboxylic acid ester, such as butene and an aldehyde, are difficult to separate from olefin, alcohol, ether and the like, and may sometimes be transferred to a reactor. In such a case, the catalyst may be conspicuously reduced in activity or extremely shortened in the life. The process for producing a lower aliphatic carboxylic acid ester of the present invention (III) using the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) can greatly decrease the production of those by-products at the stage of reaction, therefore, the present invention (III) is particularly effective in the case where the above-described recycling system is employed in the production process.

The present invention (IV) is described below. The present invention (IV) is a process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which process comprises the following first to fourth steps:

First Step

a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst;

Second Step

a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in the reaction of a lower olefin with a lower aliphatic carboxylic acid in a gas phase;

Third Step

a step of contacting the heteropolyacid salt supported catalyst filled in the reactor, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and

lower aliphatic alcohols; and

Fourth Step

5 a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester.

10 The first step is described below. The first step in the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV) is a step of loading a heteropolyacid salt on a support to obtain a heteropolyacid salt supported catalyst.

15 The heteropolyacid salt and the support used in the first step, the method for loading the heteropolyacid salt on a support performed in the first step, the method for measuring the amount of the heteropolyacid salt supported, and the preferred amount of the heteropolyacid salt supported on a support may be the same as in the present invention (I).

20 The second step is described below. The second step in the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV) is a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase.

25 The second step is a step of filling the heteropolyacid salt supported catalyst into a reactor for use in the reaction of a lower olefin with a lower aliphatic carboxylic acid, so that the second step of the present invention (I) which is the catalyst for use in producing a lower aliphatic carboxylic acid ester, or the second step of the present invention (II) which is the process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, namely, a step of contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least

one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, can be performed in the reactor without using another vessel.

5 The reactor used in the second step is not particularly limited. A fixed bed gas phase-type reactor is preferred, and a reactor having a form of multi-tube system and/or multi-layer system is more preferred. In
10 general, a reactor having a form of multi-tube system and/or multi-layer system is superior in the reaction results, thermal efficiency, eases of control and the like. Of course, the present invention is not limited thereto.

 In the present invention, the term "filling the
15 catalyst into a reactor" refers to placing the catalyst in a predetermined site of the reactor. The site and the method for the placement and in the case where the reactor uses a fixed bed system, the method for fixing the catalyst may vary depending on the form of the
20 reactor and these are not particularly limited. Specific examples of the reactor include Fig. C-4-43 "Methanol Treating Gas Phase Reactor" in the item of "4) Fixed catalyst gas phase reactor", described in Kagaku Sochi Binran (Chemical Apparatuses Handbook), 2nd ed., 3rd
25 imp., pp. 905 to 906, edited by Society of Japan Chemical Engineering, published by Maruzen (February 20, 1980).

 The third step is described below. The third step in the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV) is a step of
30 contacting a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols with the heteropolyacid salt supported catalyst filled in the reactor.

35 The method for contacting the catalyst with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and

lower aliphatic alcohols performed in the third step, the conditions such as temperature, pressure, space velocity and time, the lower aliphatic carboxylic acid and lower aliphatic alcohol used for the gas, and the compositional ratio of the gas to which water is further added, may be the same as the second step of the present invention (I).

In performing the contacting in the reactor, the conditions therefor are not particularly limited, and the preferred conditions are considered to vary depending on the form, shape, size or constructive material of the reactor used for the contacting. In general, the contacting may be performed under the conditions described above for the second step of the present invention (I).

The fourth step is described below. The fourth step of the present invention (IV) is a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester.

The lower olefin and lower aliphatic carboxylic acid used in the fourth step, the amount ratio thereof, the conditions such as addition of water, temperature, pressure and GHSV on performing the fourth step, and the recycling operation mainly of the unreacted lower olefin may be the same as in the process for the producing a lower aliphatic carboxylic acid ester of the present invention (III).

The third step and the fourth step of the present invention (IV) may or may not be clearly distinguished. Examples of the practical embodiment having a clear distinction between both steps include the case where after judging that the contacting in the third step is finished, the flow of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols is once stopped or the temperature is further lowered to

complete the third step and, thereafter, the starting material gas containing a lower olefin and a lower aliphatic carboxylic acid is passed as the reaction gas in the fourth step.

5 Examples of the practical embodiment not having a clear distinction between the two steps include the case where, after judging that the contacting in the third step is finished, while not once stopping the flow of the gas containing at least one member selected from the
10 group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols or by adjusting the temperature to the range suitable for the fourth step to prepare the initiation of reaction, the starting material gas containing a lower olefin and a lower aliphatic
15 carboxylic acid is passed as the reaction gas in the fourth step.

 For example, in the case where the lower aliphatic carboxylic acid used for the contacting in the third step is a lower aliphatic carboxylic acid corresponding to the
20 ester as an objective product of the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV), the reaction may be performed according to the practical embodiment not having a clear distinction between the third step and the fourth step.
25 On the other hand, in the case where the lower aliphatic carboxylic acid used for the contacting in the third step is not a lower aliphatic carboxylic acid corresponding to the objective ester, the reaction is preferably performed by providing a clear distinction between those two steps.

30 In general, the contacting in the third step is preferably performed using a lower aliphatic carboxylic acid corresponding to the ester as an objective product of the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV). For example,
35 in the case of producing ethyl acetate as the lower aliphatic carboxylic acid ester by applying the process for producing a lower fatty acid ester of the present

invention (IV), one of the preferred practical
embodiments is a method of performing the contacting in
the third step using a mixed gas of water and acetic acid
for a constant time under constant conditions, then
5 varying various conditions within the reactor, such as
temperature, pressure and GHSV, to fit the production
process of a lower aliphatic carboxylic acid ester, and
adding ethylene to the gas introduced into the reactor.
Of course, the present invention (IV) is not limited
10 thereto.

The present invention will be further illustrated
below by referring to the Examples and Comparative
Examples, however, the present invention should not be
construed as being limited thereto.

15 Conditions for Analysis of Metal in Support

The analysis of metals in the support was performed
using a fluorescent X-ray analyzer (PW2404, manufactured
by PHILIPS). Measurement conditions - atmosphere:
helium, effective diameter: 25.0 mm, and matrix: 2 SiO₂.

20 Conditions for Analysis of Uncondensed Gas

The analysis was performed under the following
conditions using an absolute calibration curve process by
sampling 50 ml of the effluent gas and passing the entire
amount thereof into a 1 ml gas sampler attached to the
gas chromatograph.

25 1. Ether, Carboxylic Acid Ester, Alcohol and Trace By-
Products

Gas chromatography:

gas chromatography (GC-14B, manufactured by
Shimadzu Seisakusho Co.) with a gas sampler
for Shimadzu gas chromatograph (MGS-4,
measuring tube: 1 ml)

Column: packed column SPAN 80, 15% Shinchrom A of 60
to 80 mesh (length: 5 m)

Carrier gas: nitrogen (flow rate: 25 ml/min)

Temperature conditions:

The detector and the vaporization chamber were at a temperature of 120°C, and the column temperature was 65°C and constant.

Detector: FID (H₂ pressure: 60 kPa, air pressure: 100 kPa)

2. Butene

Gas chromatography:

gas chromatography (GC-14B, manufactured by Shimadzu Seisakusho Co.) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unicarbon A-400 of 80/100 mesh, length: 2 m

Carrier gas: helium (flow rate: 23 ml/min)

Temperature condition:

The detector and the vaporization chamber were at a temperature of 130°C, and the column temperature was elevated from 40°C to 95°C at a temperature rising rate of 40°C/min.

Detector: FID (H₂ pressure: 70 kPa, air pressure: 100 kPa)

3. Ethylene

Gas chromatography:

gas chromatography (GC-14B, manufactured by Shimadzu Seisakusho Co.) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unibeads IS, length: 3 m

Carrier gas: helium (flow rate: 20 ml/min)

Temperature condition:

The detector and the vaporization chamber were at a temperature of 120°C, and the column temperature was 65°C and constant.

Detector: TCD (He pressure: 70 kPa, current: 90 mA,

- 32 -

temperature: 120°C)

Analysis of Solution Collected

The analysis was performed using an internal standard method by injecting 0.4 μ l of an analysis solution obtained by adding 1 ml of 1,4-dioxane as an

5 internal standard to 10 ml of the reaction solution.

Gas chromatography:

GC-14B manufactured by Shimadzu Seisakusho Co.

Column: capillary column TC-WAX (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μ m)

Carrier gas: nitrogen (split ratio: 20, column flow rate: 1 ml/min)

Temperature condition:

The detector and the vaporization chamber were at a temperature of 200°C, and the column temperature was kept at 50°C for 5 minutes from the starting of analysis, then elevated to 150°C at a temperature rising rate of 20°C/min, and kept at 150°C for 10 minutes.

Detector: FID (H_2 pressure: 70 kPa, air pressure: 100 kPa)

Support

Support 1: synthetic silica (N-602T, produced by Nikki Kagaku K.K.) (specific surface area: 132 m^2/g , pore volume: 0.7 cm^3/g)

Support 2: synthetic silica (CARiACT Q-10, produced by Fuji Silicia Kagaku K.K.) (specific surface area: 219.8 m^2/g , pore volume: 0.660 cm^3/g)

Support 3: natural silica (KA-160, produced by Sud Chemie AG) (specific surface area: 130 m^2/g , pore volume: 0.53 cm^3/g)

Support 4: natural silica (KA-0, produced by Sud Chemie AG) (specific surface area: 68.5 m^2/g , pore volume: 0.71 cm^3/g)

- 33 -

Support 5: silica gel (Wakogel C-200, produced by Wako Junyaku Kogyo K.K.) (specific surface area: 762 m²/g, pore volume: 0.23 cm³/g)

The metal analysis results of each support are shown in Table 1.

Table 1

	SiO ₂	K ₂ O	Na ₂ O	CaO	Cr ₂ O ₃	Fe ₂ O ₃	MgO	ZrO ₂	TiO ₂	Al ₂ O ₃	SrO	Nb ₂ O ₅	Rb ₂ O
1 Support 1	99.316	0.009	0.319	0.112	0.002	0.032	0.052	0.010	0.028	0.120	0.001	-	-
2 Support 2	99.863	-	0.021	0.040	-	0.005	0.040	0.005	0.025	-	-	-	-
3 Support 3	97.142	0.276	0.008	0.109	0.002	0.284	0.178	0.040	0.234	1.720	-	0.004	0.003
4 Support 4	98.963	0.057	0.049	0.085	0.001	0.113	0.077	0.023	0.180	0.445	-	0.005	0.001
5 Support 5	99.917	-	-	0.032	-	-	0.020	0.005	0.027	-	-	-	-

Unit: mass%

Preparation Process of Catalyst 1

Support 1 was preliminarily dried for 4 hours in a (hot-air type) drier previously adjusted to 110°C. After the preliminary drying, 1 liter of the support was measured on the bulk density using a 1 liter measuring cylinder. Tungstosilicic acid was weighed to the amount shown in Table 2 and after adding thereto 15 ml of pure water, uniformly dissolved. To this impregnating solution, pure water was further added to make the liquid amount shown in Volume of Solution Prepared of Table 2. Thereafter, the preliminarily dried support was weighed to the amount shown in Table 2, added to the impregnating solution and impregnated with the solution while thoroughly stirring. The support impregnated with the solution was transferred to a porcelain dish, air-dried for 1 hour and then dried in a hot-air type drier adjusted to 150°C for 5 hours. After the drying, the catalyst was transferred in a desiccator and left standing to cool to room temperature. This is designated as a "tungstosilicic acid supported catalyst".

Subsequently, lithium nitrite was weighed to the amount shown in Table 2 and after adding thereto 15 ml of pure water, uniformly dissolved. To this impregnating solution, pure water was added to make the liquid amount shown in Volume of Solution Prepared shown of Table 2 and then the solution was uniformly stirred. The tungstosilicic acid supported catalyst after cooling was added, in the entire amount, to the impregnating solution and impregnated with the solution while thoroughly stirring. The support impregnated with the solution was transferred to a porcelain dish, air-dried for 1 hour and then dried in a hot-air type drier adjusted to 150°C for 5 hours. After the drying, the catalyst was transferred in a desiccator and left standing to cool to room temperature. The weight of the thus-obtained catalyst was measured.

The result is also shown in Table 2.

Table 2

Catalyst Name	Support	Bulk Density (g/l)	Weight of Support (g)	Kind of Catalyst Component	Amount of Catalyst Component (g)	Kind of Neutralization Salt	Amount of Neutralization Salt (g)	Volume of Solution Prepared (ml)	Weight after Drying (g)
Catalyst 1	Support 1	813	81.3	HSiW	46.51	LiNO ₃	0.0958	69	121.4
Catalyst 2	Support 1	813	81.3	HSiW	40.70	NaOAc	0.0998	69	116.8
Catalyst 3	Support 2	456	45.6	HSiW	40.70	LiNO ₃	0.0838	43	80.8
Catalyst 4	Support 3	575	57.5	HSiW	34.88	Cu(NO ₃) ₂	0.3421	32	87.9
Catalyst 5	Support 1	813	81.3	HPW	47.51	LiNO ₃	0.0917	69	121.5
Catalyst 6	Support 4	558	55.8	HPW	65.32	NaNO ₃	0.1623	34	111.3
Catalyst 7	Support 1	813	81.3	HPW	53.44	NaNO ₃	0.1328	69	126.7
Catalyst 8	Support 4	558	55.8	HSiW	34.88	LiNO ₃	0.1078	34	86.1
Catalyst 9	Support 5	1045	104.5	HSiW	34.88	Cu(NO ₃) ₂	0.2933	31	134.2

HPW: H₃PW₁₂O₄₀HSiW: H₄SiW₁₂O₄₀

Preparation Process of Catalyst 2

Support 1 was preliminarily dried for 4 hours in a (hot-air type) drier previously adjusted to 110°C. After the preliminary drying, 1 liter of the support was measured on the bulk density using a 1 liter measuring cylinder. Tungstosilicic acid and sodium acetate each was weighed to the amount shown in Table 2 and after adding thereto 15 ml of pure water, uniformly dissolved to obtain an aqueous solution of $\text{Na}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$ (impregnating solution). To this impregnating solution, pure water was further added to make the liquid amount shown in Volume of Solution Prepared of Table 2. Thereafter, the preliminarily dried support was weighed to the amount shown in Table 2, added to the impregnating solution and impregnated with the solution while thoroughly stirring. The support impregnated with the solution was transferred to a porcelain dish, air-dried for 1 hour and then dried in a hot-air type drier adjusted to 150°C for 5 hours. After the drying, the catalyst was transferred in a desiccator and left standing to cool to room temperature. The weight of the thus-obtained catalyst was measured.

The result is also shown in Table 2.

Preparation Process of Catalysts 3, 5 and 7

These catalysts were prepared by changing the kind and weight of the support, the kind and weight of the catalyst component, and the weight of the neutralization salt as shown in Table 2 in Preparation Process of Catalyst 1. The loading on a support was performed in the same manner as in Preparation Process of Catalyst 1.

The results are also shown in Table 2.

Preparation Process of Catalysts 4 and 6

These catalysts were prepared by changing the kind and weight of the support, the kind and weight of the catalyst component, and the weight of the neutralization salt as shown in Table 2 in Preparation Process of Catalyst 2. The loading on a support was performed in

the same manner as in Preparation Process of Catalyst 2.

The results are also shown in Table 2.

Preparation Process of Catalyst 8

Support 4 was preliminarily dried for 4 hours in a
5 (hot-air type) drier previously adjusted to 110°C. After
the preliminary drying, 1 liter of the support was
measured on the bulk density using a 1 liter measuring
cylinder. Lithium nitrate was weighed to the amount
shown in Table 2 and after adding thereto 15 ml of pure
10 water, uniformly dissolved. To this impregnating
solution, pure water was further added to make the liquid
amount shown in Volume of Solution Prepared of Table 2.
Thereafter, the preliminarily dried support was weighed
to the amount shown in Table 2, added to the impregnating
15 solution and impregnated with the solution while
thoroughly stirring. The support impregnated with the
solution was transferred to a porcelain dish, air-dried
for 1 hour and then dried in a hot-air type drier
adjusted to 150°C for 5 hours. After the drying, the
20 catalyst was transferred in a desiccator and left
standing to cool to room temperature. This is designated
as a "lithium nitrate supported catalyst".
Tungstosilicic acid was weighed to the amount shown in
Table 2 and after adding thereto 15 ml of pure water,
25 uniformly dissolved.

To this impregnating solution, pure water was added
to make the liquid amount shown in Volume of Solution
Prepared shown of Table 2 and then the solution was
uniformly stirred. The lithium nitrate supported
30 catalyst was added in the entire amount to the
impregnating solution and impregnated with the solution
while thoroughly stirring. The lithium nitrate supported
catalyst impregnated with the solution was transferred to
a porcelain dish, air-dried for 1 hour and then dried in
35 a hot-air type drier adjusted to 150°C for 5 hours.
After the drying, the catalyst was transferred in a
desiccator and left standing to cool to room temperature.

The weight of the thus-obtained catalyst was measured.

The result is also shown in Table 2.

Preparation Process of Catalyst 9

5 This catalyst was prepared by changing the kind and weight of the support, the kind and weight of the catalyst component, and the weight of the neutralization salt as shown in Table 2 in Preparation Process of Catalyst 8. The loading on a support was performed in the same manner as in Preparation Process of Catalyst 8.

10 The result is also shown in Table 2.

Example 1

15 Into a pressure resistant vessel made of SUS 316L, 50 ml of the catalyst obtained in Preparation Process of Catalyst 1 was filled, and then contacted under the contacting conditions shown in Table 3. After the contacting, the vessel was cooled to room temperature and the catalyst used for the contacting (hereinafter referred to as "contacted catalyst") was drawn out from the vessel. Subsequently, 40 ml of the contacted catalyst was filled into a reaction tube, and a mixed gas of ethylene : acetic acid : steam : nitrogen (=78.5:8.0:4.5:9.0 by volume) was introduced thereinto at a temperature of 165°C, a pressure of 0.8 MPaG (gauge pressure) and a GHSV of 1,500 hr⁻¹, and reacted. The gas passed through the catalyst layer was collected under ice cooling for a predetermined time and the entire amount of condensed components (hereinafter referred to as a "condensed solution") was recovered and analyzed. The outlet gas remaining uncondensed (hereinafter referred to as an "uncondensed gas") was measured on the gas flow rate for the same predetermined time as in the condensed solution and then 50 ml of the gas was sampled and analyzed. The results are shown in Table 3.

Table 3

	Catalyst	Composition of Gas Treated, acetic acid: water:nitrogen (by mol)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Treating Temperature (°C)	Treating Time (hr)	Ethyl Acetate, STY (g/l-hr)	Amount of Butene Produced (vol ppm)	Trace By- Products (wt%)
Example 1	Catalyst 1	6.0:8.0:86.0	60.0	0.8	160	6	226	213	0.0113
Example 2	Catalyst 1	0.0:12.5:87.5	60.0	0.8	160	9	219	292	0.0175
		8.0:4.5:87.5				3			
Example 3	Catalyst 1	0.0:12.5:87.5	60.0	0.8	160	24	221	113	0.0053
Example 4	Catalyst 2	6.0:6.0:88.0	60.0	0.8	165	12	222	625	0.0607
Example 5	Catalyst 2	0.0:12.5:87.5	60.0	0.8	165	12	190	3174	0.4221
Example 6	Catalyst 2	12.5:0.0:87.5	60.0	0.8	165	12	219	806	0.1209
Example 7	Catalyst 3	6.0:6.0:88.0	60.0	0.8	165	12	273	106	0.0084
Example 8	Catalyst 4	6.0:6.0:88.0	60.0	0.8	165	12	215	26	0.0019
Example 9	Catalyst 5	6.0:6.0:88.0	60.0	0.8	165	12	228	59	0.0036
Example 10	Catalyst 6	6.0:6.0:88.0	60.0	0.8	165	12	203	275	0.0377
Example 11	Catalyst 7	6.0:6.0:88.0	60.0	0.8	165	12	240	102	0.0116
Example 12	Catalyst 7	6.0:6.0:88.0	40.0	0.8	165	12	235	85	0.0079
Example 13	Catalyst 7	6.0:6.0:88.0	20.0	0.8	165	12	230	61	not detected
Example 14	Catalyst 7	6.0:6.0:88.0	60.0	0.8	165	1	231	1224	0.0832
Example 15	Catalyst 8	6.0:6.0:88.0	60.0	0.8	165	8	181	200	0.0148
Example 16	Catalyst 9	6.0:6.0:88.0	60.0	0.8	165	8	174	189	0.0130

Examples 2 and 3

In the same manner as in Example 1, 50 ml of the catalyst obtained in Preparation Process of Catalyst 1 was filled into a pressure resistant vessel made of SUS 316L and contacted under the contacting conditions shown in Table 3. Thereafter, the catalyst was drawn out, filled into a reaction tube and then subjected to a reaction in the same manner. The results are shown in Table 3.

Example 4

Into a reaction tube, 40 ml of the catalyst obtained in Preparation Process of Catalyst 2 was filled and contacted under the contacting conditions shown in Table 3. Subsequently, a mixed gas of ethylene : acetic acid : steam : nitrogen (=78.5:8.0:4.5:9.0 by volume) was introduced thereinto at a temperature of 165°C, a pressure of 0.8 MPaG (gauge pressure) and a GHSV of 1,500 hr⁻¹, and reacted. The reaction results are shown in Table 3.

Examples 5 to 16

In the same manner as in Example 4, 40 ml of the catalyst shown in Table 3 was filled into a reaction tube and contacted under the contacting conditions shown in Table 3. Thereafter, a reaction was performed in the same manner as in Example 5. The reaction results are shown in Table 3.

Comparative Example 1

Into a reaction tube, 40 ml of the same catalyst as in Example 1 was filled and without performing contacting, a mixed gas of ethylene : acetic acid : steam : nitrogen (=78.5:8.0:4.5:9.0 by volume) was introduced thereinto at a temperature of 165°C, a pressure of 0.8 MPaG (gauge pressure) and a GHSV of 1,500 hr⁻¹, and reacted. The gas passed through the catalyst layer was collected and analyzed in the same manner as in Example 1. The results are shown in Table 4.

Table 4

	Catalyst	Composition of Gas Treated, acetic acid: water:nitrogen (by mol)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Treating Temperature (°C)	Treating Time (hr)	Ethyl Acetate, STY (g/l-hr)	Amount of Butene Produced (vol ppm)	Trace By- Products (wt%)
Comparative Example 1	Catalyst 1	none	-	-	-	-	210	876	0.0577
Comparative Example 2	Catalyst 2	none	-	-	-	-	174	22593	2.8221
Comparative Example 3	Catalyst 3	none	-	-	-	-	268	334	0.1209
Comparative Example 4	Catalyst 4	none	-	-	-	-	205	63	0.0162
Comparative Example 5	Catalyst 5	none	-	-	-	-	224	207	0.0000
Comparative Example 6	Catalyst 6	none	-	-	-	-	191	796	0.0473
Comparative Example 7	Catalyst 7	none	-	-	-	-	228	1585	0.1454
Comparative Example 8	Catalyst 8	none	-	-	-	-	174	480	0.0281
Comparative Example 9	Catalyst 9	none	-	-	-	-	170	222	0.0294

Comparative Examples 2 to 9

In the same manner as in Comparative Example 1, 40 ml of the catalyst shown in Table 3 was filled into a reaction tube and a reaction was performed. The reaction results are shown in Table 4.

Industrial Applicability

It is apparent from the above results that in producing a lower aliphatic carboxylic acid ester from a lower olefin and a lower aliphatic carboxylic acid using a heteropolyacid salt as a catalyst, when the catalyst is contacted with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols before performing the reaction, the catalyst obtained can exhibit high initial activity and high space time yield, ensure a sufficiently long catalyst life in the practice in industry, and be greatly prevented from production of by-product compounds harmful to the catalyst, such as butene and aldehydes.

This catalyst can maintain its catalytic activity without performing the removal of by-products, therefore, the catalyst is very useful particularly in practicing the process for producing a lower aliphatic carboxylic acid ester by employing a recycling system.

CLAIMS

1. A catalyst for use in producing a lower aliphatic carboxylic acid ester, which is used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

2. The catalyst as claimed in claim 1, wherein the second step is performed in the reactor used in reacting the lower olefin with the lower aliphatic carboxylic acid in a gas phase.

3. The catalyst as claimed in claim 1 or 2, wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

4. A process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, said catalyst being used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce

a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

First Step

5 a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

10 a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

15 5. The process as claimed in claim 4, wherein the second step is performed in the reactor used in reacting the lower olefin with the lower aliphatic carboxylic acid in a gas phase.

20 6. The process as claimed in claim 4 or 5, wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid,
25 silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

7. The process as claimed in any one of claims 4 to 6, wherein the second step is performed at a temperature of 80 to 300°C.

30 8. The process as claimed in any one of claims 4 to 7, wherein the second step is performed under a pressure of 0 to 3 MPaG (gauge pressure).

35 9. The process as claimed in any one of claims 4 to 8, wherein the second step is performed at a gas hourly space velocity (GHSV) of 100 to 7,000 hr⁻¹.

10. The process as claimed in any one of claims 4 to 9, wherein the gas containing at least one member

selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is a mixed gas of water and acetic acid.

5 11. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of the catalyst as claimed in any one of claims 1 to 3.

10 12. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of water and the catalyst as claimed in any one of claims 1 to 3.

15 13. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which process comprises the following first to fourth steps:

20 First Step

a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst;

Second Step

25 a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in the reaction of the lower olefin with the lower aliphatic carboxylic acid in a gas phase;

Third Step

30 a step of contacting the heteropolyacid salt supported catalyst filled in the reactor, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols; and

35 Fourth Step

a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid

through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester.

14. The process as claimed in claim 13, wherein the
5 heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid,
10 silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

15. The process as claimed in claim 13 or 14, wherein the third step is performed at a temperature of 80 to 300°C.

16. The process as claimed in any one of claims 13 to 15, wherein the third step is performed under a pressure of 0 to 3 MPaG (gauge pressure).

17. The process as claimed in any one of claims 13 to 16, wherein the third step is performed at a gaseous
20 hourly space velocity (GHSV) of 100 to 7,000 hr⁻¹.

18. The process as claimed in any one of claims 13 to 17, wherein the lower aliphatic carboxylic acid used in the third step is the same as the lower aliphatic carboxylic acid used in producing the lower aliphatic
25 carboxylic acid ester.

19. The process as claimed in any one of claims 13 to 18, wherein the mixed gas containing a lower olefin and a lower aliphatic carboxylic acid used in the fourth step contains water.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 January 2002 (03.01.2002)

PCT

(10) International Publication Number
WO 02/00589 A3

- (51) International Patent Classification⁷: C07C 67/04, B01J 27/188
- (21) International Application Number: PCT/JP01/05532
- (22) International Filing Date: 27 June 2001 (27.06.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
2000-192964 27 June 2000 (27.06.2000) JP
60/218.803 18 July 2000 (18.07.2000) US
- (71) Applicant (for all designated States except US): **SHOWA DENKO K. K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **KADOWAKI, Etsuko** [JP/JP]; c/o Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **HIGASHI, Tomoyoshi** [JP/JP]; c/o Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **OGUCHI, Wataru** [JP/JP]; C/O Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **UCHIDA, Hiroshi** [JP/JP]; c/o Oita Plant, Showa Denko K. K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP).
- (74) Agents: **ISHIDA, Takashi** et al.; A. Aoki, Ishida & Associates, Toranomon 37 Mori Bldg., 5-1, Toranomon 3-chome, Minato-ku, Tokyo 105-8423 (JP).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report:
18 April 2002
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATALYST FOR USE IN PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER, PROCESS FOR PRODUCING THE CATALYST AND PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER USING THE CATALYST

(57) Abstract: A catalyst for use in producing a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising a step of contacting the catalyst with a gas containing at least one member selected from water, lower aliphatic carboxylic acids and lower aliphatic alcohols; a process for producing the catalyst; and a process for producing a lower aliphatic carboxylic acid ester using the catalyst. The catalyst can exhibit high initial activity and high space time yield, ensure sufficiently long catalyst life in practice in industry, and can prevent the production of by-product materials.

WO 02/00589 A3

INTERNATIONAL SEARCH REPORT

Inte. onal Application No
PCT/JP 01/05532

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C67/04 B01J27/188

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 74842 A (HIGASHI TOMOYOSHI ;KAMEI HIDEYUKI (JP); NARUMI KOUSUKE (JP); SHOWA) 14 December 2000 (2000-12-14) page 19, line 11 - line 18 claims 1-9; table 1	1-19
X	EP 0 936 210 A (BP CHEM INT LTD) 18 August 1999 (1999-08-18) claims 1-3,6-18 page 4, line 37 - line 46 page 6, line 10 - line 35 table 8	1-19
X	EP 0 959 064 A (BP CHEM INT LTD) 24 November 1999 (1999-11-24) claims 1-32	1-19
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

7 February 2002

Date of mailing of the international search report

25/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Thion, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 01/05532

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 757 027 A (BP CHEM INT LTD) 5 February 1997 (1997-02-05) claims 1-31 ----	1-19
X	DATABASE WPI Section Ch, Week 200014 Derwent Publications Ltd., London, GB; Class E17, AN 1993-252691 XP002189514 & JP 03 012059 B (SHOWA DENKO KK), 21 February 2000 (2000-02-21) abstract ----	1-19
A	WO 00 03966 A (COKER ERIC NICHOLAS ; SMITH WARREN JOHN (GB); BP CHEM INT LTD (GB);) 27 January 2000 (2000-01-27) ----	
A	EP 0 562 139 A (SHOWA DENKO KK) 29 September 1993 (1993-09-29) ----	
A	EP 0 538 826 A (MITSUI TOATSU CHEMICALS) 28 April 1993 (1993-04-28) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. onal Application No

PCT/JP 01/05532

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0074842	A	14-12-2000	JP 2000342980 A AU 4952900 A WO 0074842 A1	12-12-2000 28-12-2000 14-12-2000
EP 0936210	A	18-08-1999	BR 9900135 A CN 1232019 A EP 0936210 A1 JP 11269126 A US 6187949 B1 ZA 9900405 A	09-05-2000 20-10-1999 18-08-1999 05-10-1999 13-02-2001 20-07-2000
EP 0959064	A	24-11-1999	EP 0959064 A1 CA 2182558 A1 CN 1150585 A DE 69607536 D1 DE 69607536 T2 DE 69618032 D1 EP 0757027 A1 JP 9118647 A SG 49973 A1 US 5861530 A	24-11-1999 03-02-1997 28-05-1997 11-05-2000 08-02-2001 24-01-2002 05-02-1997 06-05-1997 15-06-1998 19-01-1999
EP 0757027	A	05-02-1997	CA 2182558 A1 CN 1150585 A DE 69607536 D1 DE 69607536 T2 DE 69618032 D1 EP 0757027 A1 EP 0959064 A1 JP 9118647 A SG 49973 A1 US 5861530 A	03-02-1997 28-05-1997 11-05-2000 08-02-2001 24-01-2002 05-02-1997 24-11-1999 06-05-1997 15-06-1998 19-01-1999
JP 3012059	B	19-02-1991	JP 1662031 C JP 62155259 A DE 3685013 D1 EP 0228846 A1 US 4762928 A	19-05-1992 10-07-1987 27-05-1992 15-07-1987 09-08-1988
WO 0003966	A	27-01-2000	AU 4632399 A BR 9912038 A CN 1309630 T EP 1097120 A1 WO 0003966 A1 US 2001047107 A1	07-02-2000 03-04-2001 22-08-2001 09-05-2001 27-01-2000 29-11-2001
EP 0562139	A	29-09-1993	US 5189201 A EP 0562139 A1	23-02-1993 29-09-1993
EP 0538826	A	28-04-1993	JP 5112491 A JP 5163200 A JP 5170699 A DE 69207705 D1 DE 69207705 T2 EP 0538826 A2 US 5241106 A JP 5255185 A	07-05-1993 29-06-1993 09-07-1993 29-02-1996 30-05-1996 28-04-1993 31-08-1993 05-10-1993